

Calculation of the Admittance Function for a Burning Surface

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Abstract—Calculation of the Admittance Function for a Burning Surface. A thorough analysis of pressure oscillations in a solid propellant rocket requires specification of the response of the burning solid. Indeed, for the case of small amplitude waves, this is the most crucial aspect of the problem; unfortunately, it is also poorly understood. The admittance function is merely a convenient expression of the response which contains the primary mechanism for driving waves. In the work reported here, the usual one-dimensional approximation is made, and three main regions are distinguished: the solid phase being heated, the solid phase involving decomposition (a thin region near the surface), and the gas phase. The problem reduces simply to the solution of appropriate ordinary differential equations and satisfaction of boundary conditions, which include matching at interfaces.

The most significant differences from previous work are incorporation of a decomposition region and the treatment of the gas phase. A greatly simplified analysis of the latter leads essentially to the same results found elsewhere, but with substantially less labor. Only a quasistatic analysis, valid for frequencies less than a few thousand cycles per second, is covered, but it can be extended to higher frequencies.

Laboratory measurements have shown that the response consists generally of a single peak in the range of frequency for which the quasistatic approximation appears to be accurate. The qualitative aspects of such peaks, and their connection with 'self-excited' oscillations, are discussed. In particular, the influence of decomposition and pressure sensitivity of the various chemical reactions is examined. Limited numerical results are included.

Eventually, the aim of calculations is principally to gain some understanding of the unsteady combustion process and to aid in classifying propellants. The regions involved in the burning are separately characterized by a small number of dimensionless groups. It appears that the effects represented by these parameters may be distinguished in the response function; one may therefore be able, by use of experimental results, to determine at least qualitative connections between the response to pressure oscillations and changes of composition. In this regard, observations made in both T-burners and L* burners should prove useful.

Partial List of Symbols

Some symbols having commonly accepted meanings are not included.

| | |
|----------|---|
| A | $A = E(1 - \bar{\epsilon}_i)$; |
| c, c_p | specific heats of solid and gas; |
| D | $D = X_{-r} - X_{-o} + (1 - n_s/n)^{-1}$ $\left[P - \frac{E}{n}(X_p + X_{p-o}) \right]$; |
| E_s | activation energy for surface reaction; |
| E | $E = E_s/R\bar{T}_s$; |
| H_p | latent heat for surface reaction; $H_p > 0$ for exothermic surface reaction; |

| | |
|-------------|---|
| H | $H = H_p/c\bar{T}_s$; |
| l | normalized thickness of decomposition region; |
| L_1, L_2 | defined after Eq. (29); |
| \bar{m} | average mass flux; |
| m'_s | fluctuation of mass flux at the surface; |
| n | index in the linear burning rate law, $r = ap^n$; |
| n_s | index in the surface pyrolysis law, Eq. (10); |
| P | $P = (E/n)(c_p/c)q_2$; |
| \dot{Q}_d | average heat release (per unit volume) in solid; |
| Q | $Q = \dot{Q}_d\lambda_p/\bar{T}_s(\bar{m}c)^2$; |
| Q_g | normalized heat release in gas phase: $Q_g = \dot{Q}_g/(\bar{m}c_p)^2\bar{T}_s$; |
| $q'_{0\pm}$ | fluctuations of heat transfer at the |

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|---|--|
| | average position of the surface ($x = 0$); |
| $q'_{s\pm}$ | fluctuations of heat release at the surface; |
| q_1, q_2 | defined in Eq. (34); |
| r | linear burning rate; |
| T_i | initial temperature of propellant ($x \rightarrow -\infty$); |
| T_s | temperature of burning surface; |
| T_l | temperature at cold edge of decomposition region; |
| \bar{T}_c | average chamber temperature ($x \rightarrow +\infty$); |
| x_s, \dot{x}_s | surface displacement, velocity; |
| X_+, X_-, X_s | functions defined in Eqs. (31) and (37); |
| X_{p-}, X_p | functions defined in Eqs. (32) and (37); |
| α, β | functions defined after Eq. (29); |
| $\alpha_0, \alpha_1, \beta, A_{10}, X_{-0}, L_{11}$ | constants defined in Appendix D; |
| Δ_l | $(\Delta_l = \bar{T}_l - T_i)/\bar{T}_s$; |
| δ_r | Eq. (21); |
| δ_s | replaces δ_r in Eq. (25); |
| ϵ | stands for p'/\bar{p} ; |
| λ_1, λ_2 | defined after Eq. (27); |
| λ_p, λ_g | thermal conductivities of solid and gas; |
| A_1 | $A_1 = L_1 + L_2$; |
| μ | stands for $(m'_s/\bar{m})_r$; |
| ρ_p, ρ | density of solid propellant and gas phase; |
| $\bar{\rho}_c$ | average density in chamber; |
| σ_1, σ_2 | defined in Eq. (19); |
| τ | normalized temperature; |
| ω_p, ω_g | frequency parameters for the solid and gas phases; |
| $(\bar{})$ | mean value; |
| $()'$ | fluctuating value; |
| $()_s$ | evaluated at the solid-gas interface; |
| $()_{s\pm}$ | evaluated on the gas (+) or solid (-) side; |
| $()_{0\pm}$ | evaluated on the gas or solid side of the mean position of the burning surface; |
| $()_{l\pm}$ | evaluated on the positive or negative side of the cold boundary of the decomposition region; |
| $()_r$ | real part; |
| $()_i$ | imaginary part. |

Introduction

THE PRIMARY driving of oscillations in a solid propellant rocket chamber is associated with the inter-

action between motions in the gas phase and the combustion process at the propellant surface. Either fluctuations of pressure, or of velocity parallel to the surface, may couple the burning and the waves. It appears, however, that these two effects are often not of comparable influence simultaneously. Hence, one is justified in treating them separately; here, considerations will be limited to 'pressure coupling' which must in any case be present. As a convenience, the process is usually interpreted in terms of an admittance function, the ratio of normal velocity fluctuation to the pressure fluctuation. The results are useful for studying the stability of acoustic modes in chambers and for interpretation of measurements made in T-burners and L^* burners.

In those cases, part of the damping constant λ is proportional to the real part of the complex admittance function. The reason for this is that the real part gives the portion u'_r of the velocity fluctuation which is in phase with the pressure oscillation, p' . Locally, the contribution to the damping constant is proportional to $u'_r p'$, which is simply the rate at which work (' $p-v$ ' work) is done on the waves by the burning surface. According to the definition of the admittance function A_b , this product is simply $A_b^{(r)} p'^2$ where $A_b^{(r)}$ is the real part of A_b . For steady waves, the average rate at which work may be done by the burning surface is therefore proportional to $A_b^{(r)}$. Hence, the larger is the real part of the admittance function, the greater is the tendency for the waves to be sustained. It is important to realize, however, that this quantity alone is not a satisfactory measure of stability; there is another contribution of comparable magnitude, associated with the mean flow at the surface.¹ The two effects must be considered together for a meaningful assessment of stability.

Several studies of this problem [1-5] exist, but there remains a significant gap between analyses and experimental results. Moreover, it is difficult to gain an intuitive feeling for the situation because much tends to be obscured in the calculations. Actually, the various treatments differ from one another in two respects only: the choice of coordinate system and, more importantly, the analysis of the gas phase. But attempts to offer generalizations are inevitably hindered by the large number of parameters and by the various approximations. On the other hand, it appears futile to expect accurately detailed quantitative results. Approximations are necessary, and much of

¹ This would be non-zero in the absence of combustion as, for example, would be the case if flow through a porous wall were maintained by external means.

the basic information one would like to have, notably about the chemical kinetics involved, is simply not known. Thus, for design purposes, it seems best at this time to try to characterize, somehow, the gross aspects of the problem.

There are three obviously main parts of the problem: the solid phase, the surface region, and the gas phase. One purpose here is to show the very important influence of a decomposition region within the solid phase. Initially, the motivation for including what appears to be just one more complication was the experimental result that large peaks in the response function occur in the frequency range up to about 1 kc [6]. This is well below frequencies at which one would expect the gas phase to respond in such a manner. The peaks seemed to be larger and of somewhat different character than could be obtained from a model in which the solid is simply heated before vaporization at the surface. Sensitivity of the decomposition process does indeed affect response in the region of the maximum, but not in the manner anticipated. For the treatment followed here, one can in fact find very large maxima (infinite values in some cases) in the limit of no decomposition. The peaks are reduced and smoothed out if decomposition is included.

In the decomposition reactions and the surface reaction are permitted to be sensitive to changes of pressure, the response is reduced substantially. This is perhaps contrary to what one might expect, and is due to an indirect influence, tending to reduce the surface temperature or increase the heat transferred away from the surface.

A very simple treatment of the gas phase is given, valid in the limit of 'quasi-static' behavior, when the gas phase responds very quickly relative to the solid phase. It appears to be a good approximation for real frequencies up to (at least) several thousand cycles per second. The entire analysis is put in such a form that it is not difficult to trace the influences that the various parts of the problem have ultimately on the admittance function.

No attempt is made to compare the results with experimental data, and only a limited amount of numerical results are included. However, the separate regions are individually characterized by a relatively small number of parameters which, when suitably varied, can be used usefully in a study of data. It appears that the response function is sensitive to variations of the parameters in such a way that it might be possible to distinguish the influences of the regions (solid, surface, gas) in the measurements. In this way, one might find at least a partial explanation for the observed dependence of the response on small

changes of composition. It is far from clear at present whether unambiguous comparisons can be made.

Formulation: Equations and Boundary Conditions

Much of the formulation adopted is identical with earlier practices. In particular, the problem is taken to be one-dimensional and all material properties are treated as quantities averaged over the chemical composition. Thus, in the first instance, one seems restricted to double-base propellants. But in fact the same treatment may apply to composite propellants, providing one can determine how to average as well over space, particle size, etc. This subject is not pursued here.

It is important, however, that the coordinate system used for the time-varying problem be clearly defined and understood. Some authors have chosen a system attached *always* to the burning surface. Hence, it is not an inertial system and the usual equations of motion for the gas phase are not precisely valid. Indeed, some (numerically unimportant) terms of order ρ/ρ_p are tacitly ignored in all those works. It seems better to use an inertial system [4], in this case, with the origin at the mean position of the burning surface. The solid appears to be moving from the left at the steady linear burning rate (Fig. 1). One has then to be careful with the boundary conditions at the interface between the solid and gas.

The temperature of the solid is governed by

$$\lambda_p \frac{\partial^2 T}{\partial x^2} - \bar{m}c \frac{\partial T}{\partial x} - \rho_p c \frac{\partial T}{\partial t} = -\dot{Q}_d \quad (1)$$

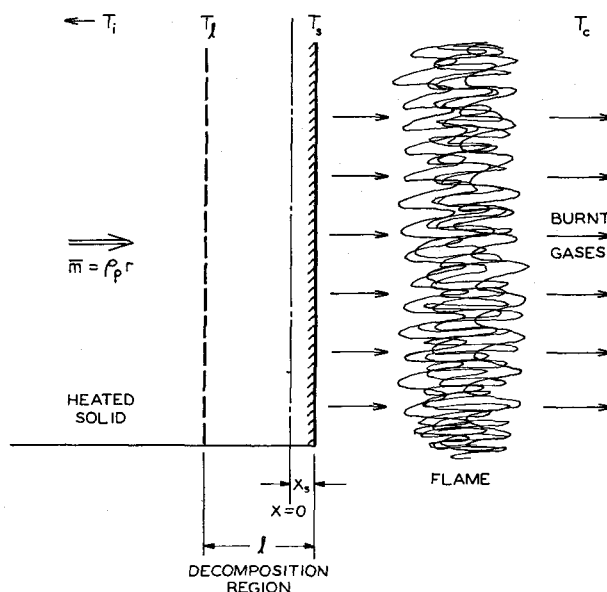


FIG. 1. Sketch of the model.

with \dot{Q}_d the rate of heat generation per unit volume ($\dot{Q}_d = 0$ outside the decomposition region). Note that in the convective term, $\bar{m} = \rho_p r$ is fixed always, and is independent of time for the coordinate system of Fig. 1. The equations for the gas phase are more involved, particularly if one accounts for diffusion. One way of writing the conservation equations for mass, concentration of individual species, and energy is:

$$\frac{\partial \rho}{\partial t} + \frac{\partial m}{\partial x} = 0 \quad (2)$$

$$\rho \frac{\partial K_i}{\partial t} + \rho u \frac{\partial K_i}{\partial x} - \frac{\partial}{\partial x} \left(\rho D \frac{\partial K_i}{\partial x} \right) = w_i \quad (3)$$

$$\begin{aligned} \rho \frac{\partial h}{\partial t} + \rho u \frac{\partial h}{\partial x} - \frac{\partial}{\partial x} \left(\frac{\lambda_g}{c_p} \frac{\partial h}{\partial x} \right) \\ = \frac{\partial p}{\partial t} + \frac{\partial}{\partial x} \left[\frac{\lambda_g}{c_p} (Le - 1) \sum h_i^0 \frac{\partial K_i}{\partial x} \right] \end{aligned} \quad (4)$$

where the enthalpy is

$$h = \sum K_i h_i$$

and for each species,

$$h_i = \int_0^T c_{pi} dT + h_i^0.$$

If one uses the approximation that the Lewis number (Le) is unity, $Le = k/\rho c_p D = 1$ and the energy equation for the gas phase is

$$\frac{\partial}{\partial x} \left(\lambda_g \frac{\partial T}{\partial x} \right) - mc_p \frac{\partial T}{\partial x} - \rho c_p \frac{\partial T}{\partial t} = -\dot{Q} - \frac{\partial p}{\partial t}. \quad (5)$$

The symbol \dot{Q} stands for the local rate of heat released per unit volume,

$$\dot{Q} = - \sum w_i h_i^0.$$

Since the thickness of the burning region is much less than a wavelength, and the flow speed is much less than the speed of sound, the conservation of momentum may be replaced by the statement that the pressure is approximately uniform throughout the region of interest.

Deep in the solid, the temperature must become the constant temperature of the propellant, independently of time:

$$T \rightarrow T_i \quad (x \rightarrow -\infty) \quad (6)$$

Far from the surface in the gas phase, the mean temperature is the chamber temperature, \bar{T}_c , and the oscillating temperature approaches that of an acoustic wave, assumed to be isentropic:

$$T' \rightarrow \frac{\gamma - 1}{\gamma} \bar{T}_c \frac{p'}{p} \quad (x \rightarrow +\infty). \quad (7)$$

The physical conditions at the solid-gas interface may be deduced by considering a small control volume about the true burning surface located at $x = x_s$ and moving with speed \dot{x}_s , as illustrated in Fig. 2. One finds for the conservation of unsteady mass flux and total energy transfer:

$$\frac{\rho_p \dot{x}_s}{\bar{m}} = - \left(1 - \frac{\bar{\rho}}{\rho_p} \right)^{-1} \frac{m'_s}{\bar{m}} \quad (8)$$

$$\begin{aligned} \lambda_g \left(\frac{\partial T}{\partial x} \right)_{s+} &= \lambda_p \left(\frac{\partial T}{\partial x} \right)_{s-} \\ &+ \bar{m} \left(1 - \frac{\rho_p \dot{x}_s}{\bar{m}} \right) [-H_p + (c_p - c) T_s] \end{aligned} \quad (9)$$

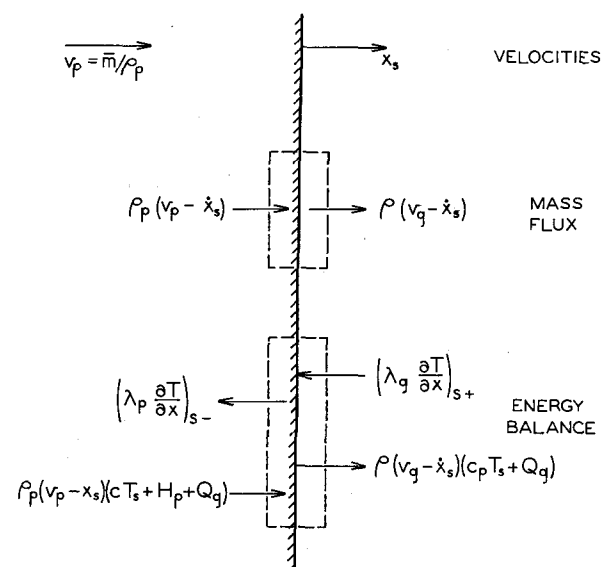


FIG. 2. Control volumes for matching conditions at the solid-gas interface.

For an exothermic surface reaction, the latent heat H_p is positive as defined here. A law relating the conversion of solid to gas, to surface characteristics, is required. If an Arrhenius law is used,

$$m_s = B p^{n_s} \exp [- E_s / RT_s],$$

then

$$\frac{m'_s}{\bar{m}_s} = \frac{E_s}{RT_s} \frac{T'_s}{T_s} + n_s \frac{p'}{p}. \quad (10)$$

There are two assumptions involved here: first, that the Arrhenius law governs the process; and second, that the responses to both temperature and pressure changes occur without additional time lags. Thus, for example, even if the Arrhenius law were precisely

correct for steady conditions, dynamically the process might be better represented as

$$\frac{m'_s}{\bar{m}} = \frac{E_s}{R\bar{T}_s} \frac{T'_s}{\bar{T}} e^{i\phi_1} + n_s \frac{p'}{\bar{p}} e^{i\phi_2} \quad (11)$$

in which ϕ_1, ϕ_2 are unknown phases measured with respect to the pressure oscillation outside the flame region. (It should be remarked that T'_s/\bar{T} is itself a complex function, as later results show—changes of surface temperature, in general, lag or lead the pressure changes, depending on the frequency.) Nothing is known about this aspect of the chemical kinetics, and therefore ϕ_1 and ϕ_2 are simply ignored, although they could be retained as two more parameters. The first assumption is really not very restrictive; for a problem involving small temperature and pressure changes, Eq. (10) expresses the assumption that m'_s depends on T'_s and p' and hence two parameters are introduced. For an Arrhenius law, the two parameters happen to be $E_s/R\bar{T}_s$ and n_s , but since they are not known in any case, and will be varied, the statement that an Arrhenius law is assumed should not be taken too seriously.

From the solutions for temperature in the solid and gas phase, one obtains the fluctuation values of temperature and temperature gradient on $x = 0$. The values on $x = x_s$ are set in the usual manner of treating linearized boundary conditions. Thus, one has

$$T'_s = T'_{o\pm} + x_s \left(\frac{dT'}{dx} \right)_{o\pm} \quad (12)$$

$$\left(\frac{\partial T'}{\partial x} \right)_{s\pm} = \left(\frac{\partial T'}{\partial x} \right)_{o\pm} + x_s \left(\frac{d^2 T'}{dx^2} \right)_{o\pm} \quad (13)$$

These are really four equations, with $s\pm, o\pm$ denoting the gas and solid sides of the burning surface (s) and the origin (o). The right-hand sides of Eqs. (12) and (13) may be regarded as the initial terms of expansions in Taylor's series about the origin [4].

Similar equations are required for matching the decomposition region to the heated solid. Let x_i be the average position of the interface between the decomposing solid and the heated solid upstream (i.e. $x < x_i$) and let x_d be the instantaneous position. The appropriate conditions to be met are

$$T'_d = T'_{i\pm} + (x_d - x_i) \left(\frac{dT'}{dx} \right)_{i\pm} \quad (14)$$

$$\left(\frac{\partial T'}{\partial x} \right)_{d\pm} = \left(\frac{\partial T'}{\partial x} \right)_{i\pm} + (x_d - x_i) \left(\frac{d^2 T'}{dx^2} \right)_{i\pm} \quad (15)$$

The procedure followed here is first to solve the

problems for the solid and gas phases separately. One obtains expressions for the heat transfer, to the two sides of the solid-gas interface, in terms of the surface temperature and pressure fluctuations. These are inserted in the energy matching condition to yield a formula for the ratio of surface temperature to pressure fluctuation. Subsequently, the oscillation of mass flux and admittance function may be found.

Solution for the Solid Phase

It is clearly better to work with dimensionless variables; hereafter, τ will stand for the temperature divided by the mean surface temperature (\bar{T}_s) and the coordinate variable in the solid phase is $\xi_p = \bar{m}cx/\lambda_p$. Thus, ξ_{pl} and ξ_{pd} stand for the mean and instantaneous positions of the boundary between the region where solid is being heated and the decomposition region. The equation governing the mean temperature is therefore

$$\frac{d^2 \bar{\tau}}{d\xi_p^2} - \frac{d\bar{\tau}}{d\xi_p} = \begin{cases} 0 & \xi_p < \xi_{pl} \\ -Q & \xi_p > \xi_{pl} \end{cases}$$

with $Q = \dot{Q}_d \lambda_p / \bar{T}_s (\bar{m}c)^2$. Material properties (c, ρ_p, λ_p) are assumed to be uniform throughout the solid phase. For simplicity, Q will be assumed constant at some average value. The solutions satisfying $\bar{\tau} = \bar{\tau}_i$ for $\xi_p \rightarrow -\infty$, $\bar{\tau} = 1$ for $\xi_p = 0$, and continuity of heat transfer at $\xi_p = \xi_{pl} = -l$ are

$$\bar{\tau} = \bar{\tau}_i + \Delta_l e^{\xi_p + l} \quad (\xi_p < -l) \quad (16)$$

$$\bar{\tau} = 1 - (Q + \Delta_l) e^l + (Q + \Delta_l) e^{\xi_p + l} - Q \xi_p \quad (-l < \xi_p < 0) \quad (17)$$

where $\Delta_l = (\bar{T}_i - T_i)/\bar{T}_s$. Continuity of temperature at $\xi_p = -l$ gives a condition relating Q, Δ_l and the normalized thickness, l , of the decomposition region:

$$Q = \frac{1 - \bar{\tau}_i - \Delta_l e^l}{e^l - (1 + l)}. \quad (18)$$

For the numerical calculations, this equation is probably best used to give Δ_l in terms of the remaining quantities.

If one assumes that the fluctuations of heat release are proportional to local temperature fluctuations within the decomposition region, and to the pressure changes,

$$\dot{Q}'_d = \sigma_1 \frac{T'}{\bar{T}_s} + \sigma_2 \frac{p'}{\bar{p}} \quad (19)$$

then the governing equations for harmonic temperature fluctuations are

$$\frac{d^2\tau'}{d\xi_p^2} - \frac{d\tau'}{d\xi_p} - i\frac{\omega_p}{4}\tau' = 0 \quad (\xi_p < -l) \quad (20)$$

$$\frac{d^2\tau'}{d\xi_p^2} - \frac{d\tau'}{d\xi_p} - \frac{1}{4}(i\omega_p - \delta_r)\tau' = -\frac{\kappa p'}{4\bar{p}} \quad (-l \leq \xi_p \leq 0) \quad (21)$$

with the new parameters defined as

$$\omega_p = \frac{4\lambda_p \rho_p \omega}{\bar{m}^2 c} \quad (22)$$

$$\delta_r = \frac{4\lambda_p \sigma_1}{\bar{T}_s(\bar{m}c)^2} \quad (23)$$

$$\kappa = \frac{4\lambda_p \sigma_2}{\bar{T}_s(\bar{m}c)^2} \quad (24)$$

The remarks made in connection with Eq. (11) also apply to the kinetics of heat release in the solid phase. Arbitrary phases are ignored and σ_1, σ_2 are taken to be real.

These equations for τ' can be solved, and the matching procedure outlined above carried through. However, it happens that in order to obtain proper behavior in the limit $\omega \rightarrow 0$ (see Eq. (40)), a restriction must be placed on δ_r , relating it to other quantities in the problem by a transcendental equation; it cannot be arbitrarily specified. This difficulty is avoided by assuming \dot{Q}'_d to depend on the fluctuation of surface temperature, τ'_s , an approximation which seems acceptable.¹ Equation (21) therefore becomes (δ_r is replaced by δ_s)

$$\frac{d^2\tau'}{d\xi_p^2} - \frac{d\tau'}{d\xi_p} - i\frac{\omega_p}{4}\tau' = -\frac{\delta_s}{4}\tau'_s - \frac{\kappa p'}{4\bar{p}} \quad (25)$$

The solutions for τ' in the solid are

$$\tau' = A_1 e^{\lambda_1 \xi_p} \quad (\xi_p \leq -l) \quad (26)$$

$$\tau' = A_2 e^{\lambda_1 \xi_p} + A_3 e^{\lambda_2 \xi_p} - i\frac{\delta_s}{\omega_p}\tau'_s - i\frac{\kappa p'}{\delta_p \bar{p}} \quad (-l \leq \xi_p \leq 0) \quad (27)$$

Consequently, the frequency appears only in the primary variable ω_p , which in turn enters in λ_1 and λ_2 ²:

$$\lambda_1 = \frac{1}{2}[1 + a_1 + ib_1] = \lambda_{1r} + i\lambda_{1i}$$

$$\lambda_2 = \frac{1}{2}[1 - a_1 - ib_1] = \lambda_{2r} + i\lambda_{2i}$$

¹ If one assumes that \dot{Q}'_d depends on τ'_{o-} , it turns out that the limiting behavior $\omega \rightarrow 0$ is satisfied only if the coefficient of τ'_{o-} is zero.

² These are the roots of $\lambda^2 - \lambda - i\omega_p/4 = 0$ so that $i\omega_p/4 = \lambda(\lambda - 1)$; this relation is sometimes used in other works, to eliminate ω_p .

$$a_1 = \frac{1}{\sqrt{2}}[(1 + \omega_p^2)^{\frac{1}{2}} + 1]^{\frac{1}{2}}$$

$$b_1 = \frac{1}{\sqrt{2}}[(1 + \omega_p^2)^{\frac{1}{2}} - 1]^{\frac{1}{2}}$$

Now the constants A_1, A_2, A_3 may be evaluated by satisfying the condition $\tau' = \tau'_{o-}$ at $\xi_p = 0$, and by suitable matching at the boundary $\xi_p = \xi_{pd}$. That boundary will be defined by assuming the existence of a 'decomposition temperature,' analogous to an ignition temperature, below which no decomposition can take place. Therefore, the temperature fluctuation vanishes at the instantaneous position of this surface and $\tau'_d = 0$ in (14), giving

$$\tau'_{l-} + (\xi_{pd} + l)\left(\frac{d\tau'}{d\xi_p}\right)_{l-} = \tau'_{l+} + (\xi_{pd} + l)\left(\frac{d\tau'}{d\xi_p}\right)_{l+} \quad (28)$$

Moreover, conservation of energy at this interface reduces to continuity of the derivative $d\tau'/dx$, or $d\tau'/d\xi_p$. It is then a straightforward matter to use these conditions, and the expressions for τ' and $\bar{\tau}$ already found, to determine A_3 in terms of A_2 and A_1 . Finally, A_1 and A_2 are set by the conditions at $\xi_p = 0$. These manipulations are carried out in Appendix A, and the end result is the desired formula for $q'_{o-} = (d\tau'/d\xi_p)_{o-}$:

$$q'_{o-} = L_1 \tau'_{o-} + L_2 \tau'_s + \kappa \frac{L_2 p'}{\delta_s \bar{p}} \quad (29)$$

where

$$L_1 = \frac{\lambda_1 + \alpha \lambda_2}{1 + \alpha}$$

$$L_2 = i\frac{\delta_s}{\omega_p}[(1 + \beta)L_1 - \lambda_2 \beta]$$

$$\alpha = \exp[(\lambda_2 - \lambda_1)l] \frac{Q/A_1}{\lambda_2 - \lambda_1 - Q/A_1}$$

$$\beta = \exp[\lambda_2 l] \frac{\lambda_1 + Q/A_1}{\lambda_2 - \lambda_1 - Q/A_1}$$

Proper reduction to the case of no decomposition results upon setting $\bar{T}_l = \bar{T}_s$ (so $A_l \rightarrow 1 - \bar{\tau}_l$) and $\delta_s = Q = \kappa = l = 0$; one then has simply $q'_{o-} = \lambda_1 \tau'_{o-}$.

When the matching at the solid-gas interface is performed, one needs q'_{s-} and τ'_s which are given in terms of q'_{o-} and τ'_{o-} by Eqs. (12) and (13). With the mean derivatives computed from (17), one finds

$$q'_{s-} = (L_1 + L_2)\tau'_s - \xi_{ps} \times [(L_1 - 1)(Q + A_l)e^l - L_1 Q] + \kappa \frac{L_2 p'}{\delta_s \bar{p}}$$

But Eqs. (8) and (10) give

$$\xi_{ps} = -i \frac{4}{\omega_p} \left[\frac{E_s}{R \bar{T}_s} \tau'_s + n_s \frac{p'}{\bar{p}} \right]$$

and therefore

$$q'_{s-} = X_- \tau'_s + X_p \frac{p'}{\bar{p}} \quad (30)$$

with $E = E_s/R\bar{T}_s$, $A_1 = L_1 + L_2$, and

$$X_- = A_1 - i \frac{4E}{\omega_p} [(L_1 - 1)(Q + A_1)e^l - L_1 Q] \quad (31)$$

$$X_p = \frac{i}{\omega_p} \times [L_1(1 + \beta) - \lambda_2 \beta] - i \frac{4n_s}{\omega_p} [(L_1 - 1)(Q + A_1)e^l - L_1 Q] \quad (32)$$

Gas Phase

The gas phase is rigorously much more difficult to handle than the solid phase, particularly if one attempts to account for diffusion in detail. However, several reasonable approximations lead to a very simple result. All relaxation times associated with processes in the gas phase are short compared with other processes. The primary reference is of course the period of oscillations, which varies roughly from 10^{-4} to 10^{-3} sec to 10^{-1} sec for the waves usually encountered. Response times for chemical reactions depend strongly on pressure and temperature; it will be assumed here that such lags are negligible.

Through the time derivatives, the frequency arises in the analysis of the gas phase, as the dimensionless parameter ω_g :

$$\omega_g = \left(\frac{\lambda_g c \bar{p}_c}{\lambda_p c_p \rho_p} \right) \omega_p$$

For typical material properties,¹ $\lambda_g c \bar{p}_c / \lambda_p c_p \rho_p \sim O(10^{-2})$ and hence $\omega_g \ll \omega_p$: that is, the gas phase responds very much more quickly to temperature changes than does the solid. This is due primarily to the difference in density, and hence volume heat capacity. Moreover, with $\lambda_p = 5 \times 10^{-4}$ cal/sec: cm $^\circ$ K, $\rho_s = 1.5$ g/cm 3 , and $c = \frac{1}{3}$ cal/g $^\circ$ K, then $\omega_p \cong f/40 r^2$ where f is the frequency (c/s) and r is the liner burning rate (cm/sec). Most of the interesting behavior of the response seems to occur for f less than, roughly, 1000 c/s and for $r = 1$, $\omega_p \approx 25$. Hence ω_g is in fact small, although not infinitesimal; note

that ω_g decreases as the size of the rocket chamber increases.

Thus, a 'quasi-static' treatment of the gas phase is suggested: all time derivatives are ignored, and the frequency will not appear explicitly in the results. Within these approximations, then, any unusual behavior as a function of frequency must be attributed to processes in the solid, or to the conversion of solid to gas. In dimensionless form, with $\xi_g = \bar{m} c_p x / \lambda_g = (c_p \lambda_p / c \lambda_g) \xi_p$, the quasi-static form of the equations for conservation of mass and energy (Eqs. (2) and (5)) are

$$\frac{dm}{d\xi_g} = 0$$

$$\frac{d}{d\xi_g} \left\{ \frac{d\tau}{d\xi_g} - \frac{m}{\bar{m}} \tau \right\} = -Q_g$$

with $Q_g = \dot{Q} \lambda_g / (\bar{m} c_p)^2 \bar{T}_s$. The corresponding equations for the perturbations are

$$\frac{dm'}{d\xi_g} = 0$$

$$\frac{d}{d\xi_g} \left\{ \frac{d\tau'}{d\xi_g} - \tau' \right\} = -Q'_g + \frac{d}{d\xi_g} \left\{ \frac{m'}{\bar{m}} \bar{\tau} \right\}$$

Consequently, the fluctuation of mass flux is constant through the gas phase and equal to its value at the surface:

$$m' = m'_s \quad (33)$$

The first integral of the energy equation is

$$\frac{d\tau'}{d\xi_g} - \tau' = - \int_0^{\xi_g} Q'_g d\xi'_g + \frac{m'_s}{\bar{m}} (\bar{\tau} - 1) + (q'_{o+} - \tau'_{o+})$$

since $(d\tau'/d\xi_g)_{\xi_g=0} = q'_{o+}$.

A formula for q'_{o+} follows immediately by evaluating this result outside the flame region where $d\tau'/d\xi_g = 0$, τ' is given by Eq. (7), and $\bar{\tau} = \bar{\tau}_c \equiv \bar{T}_c/\bar{T}_s$.

$$q'_{o+} = + \tau'_{o+} - \frac{m'_s}{\bar{m}} (\bar{\tau}_c - 1) + \frac{\gamma - 1}{\gamma} \bar{\tau}_c \frac{p'}{\bar{p}} + \int_0^{\xi_g \rightarrow \infty} Q'_g d\xi'_g$$

Within the quasi-static approximation used here, $q'_{o+} \approx q'_{s+}$ and $\tau'_{o+} \approx \tau'_s$ (one can imagine that the gas motions respond instantaneously to the surface motions so that the corrections due to surface motion, Eqs. (12) and (13), are not relevant). In view of Eqs. (8)¹ and (9), one has

$$q'_{s+} = \tau'_s \left[1 - \frac{E_s}{R \bar{T}_s} (\bar{\tau}_c - 1) \right] - \frac{\gamma - 1}{\gamma} \bar{\tau}_c \frac{p'}{\bar{p}} + \int_0^{\infty} Q'_g d\xi'_g$$

¹ See Table 2 for a formula for \bar{p}_c .

¹ The factor $1 - \bar{p}/\rho_p$ is set equal to one.

Now the integral over Q'_g , which represents the fluctuation in heat generated within the entire gas phase, is not known. In fact, much of the laborious work previously published is concerned essentially with the problem of expressing this quantity in terms of fluctuations of pressure in temperature. But in all cases, the end result contains two additional parameters which, while they can be at least vaguely interpreted, are not precisely known. Here, it seems quite reasonable to recognize that the integral must depend linearly on τ'_s and p'/\bar{p} . This is so because locally, Q'_g is a function of temperature, pressure, and composition. For the case Lewis number equal to one, the concentrations are explicitly related to the temperature; otherwise, there is an implicit relation. But the temperature is determined by a second order equation, so that the profile will contain two end values, τ'_s and $\tau'_c = (\gamma - 1/\gamma)\bar{T}_c p'/\bar{p}$. Then one can imagine that a representation for τ' , depending on ξ_g , τ'_s , and p'/\bar{p} is inserted where needed in the function Q'_g . Hence, the integral can be formally represented as

$$\int_0^\infty Q'_g d\xi_g = q_1 \tau'_s + \left(q_2 + \frac{\gamma - 1}{\gamma} \bar{\tau}_c \right) \frac{p'}{\bar{p}}, \quad (34)$$

and the final result is

$$q'_{s+} = \left[\frac{c}{c_p} X_+ \right] \tau'_s + q_2 \frac{p'}{\bar{p}} \quad (35)$$

$$X_+ = [1 + q_1 - E(\bar{\tau}_c - 1)] \frac{c_p}{c}. \quad (36)$$

It is shown in the next section that only one of the new parameters q_1, q_2 is arbitrary if the formula for the fluctuation in mass flux is to reduce to the correct result for $\omega \rightarrow 0$.

Formula for the Admittance Function

The only step remaining is to match the result (30) and (36) by using the perturbed form of the energy balance at the surface; that condition follows from Eq. (9), with some use of (10):

$$\frac{c_p}{c} q'_{s+} = q'_{s-} + X_s \tau'_s + X_p \frac{p'}{\bar{p}} \quad (37)$$

where

$$X_s = \left(\frac{c_p}{c} - 1 \right) (E + 1) - EH$$

$$X_p = n_s \left(\frac{c_p}{c} - 1 - H \right)$$

and $H = H_p/c\bar{T}_s$. After substituting (30) and (36) into (37), one finds

$$\frac{\tau'_s}{p'/\bar{p}} = \frac{(n/E)P - (X_p + X_{p-o})}{X_- - X_+ + X_s} \quad (38)$$

so that the fluctuation of mass flux is

$$\frac{1}{n} \frac{m'_s/\bar{m}}{p'/\bar{p}} = \frac{P - E/n(X_p + X_{p-o})}{X_- - X_+ + X_s} + \frac{n_s}{n}. \quad (39)$$

The parameter $P = (E/n)(c_p/c)q_2$ contains the influence of pressure on heat release in the gas phase, and the activation energy at the surface; n is the index in the steady-state burning law $r = ap^n$.

Now in the limit $\omega \rightarrow 0$, the left-hand side of (39) must approach unity; this imposes a restriction, mentioned earlier, on q_1 and q_2 . It is best to retain q_2 (or P) as the arbitrary parameter. Indeed, if X_{-o} and X_{p-o} represent the limiting forms for $\omega \rightarrow 0$, the constraint is

$$\frac{P - (E/n)(X_p + X_{p-o})}{X_{-o} - X_+ + X_s} + \frac{n_s}{n} = 1. \quad (40)$$

This argument leading to Eq. (40) may at first seem somewhat artificial. It is, however, equivalent to satisfying the energy balance at the surface, Eq. (9), in steady state burning, which is of course the limit $\omega \rightarrow 0$. This is easily seen by using (37), the perturbed form of (9). Substitute the expressions (30) and (36) for q'_{s+}, q'_{s-} , divide the entire equation by p'/\bar{p} , and take the limit $\omega \rightarrow 0$ to find

$$(X_{-o} - X_+ + X_s) \left(\frac{\tau'_s}{p'/\bar{p}} \right)_{\omega \rightarrow 0} = \frac{c_p}{c} q - (X_p + X_{p-o}).$$

But Eq. (10) implies

$$\frac{E}{n} \left(\frac{\tau'_s}{p'/\bar{p}} \right)_{\omega \rightarrow 0} = 1 - \frac{n_s}{n}$$

and after this is inserted in the last equation, some rearrangement leads to Eq. (40). It seems best to solve that equation for $-X_+ + X_s$ and substitute into (39), giving the formula

$$\begin{aligned} \frac{1}{n} \frac{m'_s/\bar{m}}{p'/\bar{p}} &= \frac{P - \frac{E}{n}(X_p + X_{p-o})}{(X_- - X_{-o}) + \frac{1}{1 - n_s/n} \left[P - \frac{E}{n}(X_p + X_{p-o}) \right]} \\ &\quad + \frac{n_s}{n}. \end{aligned} \quad (41)$$

It is a curious result that q_1 , related to that part of the heat release in the gas phase which depends on

temperature, does not appear in the final result, and H_p , the latent heat for the phase change at the surface, appears only if the surface reaction depends on the pressure. Such a conclusion seems implicit also in previous works. In the work of Denison and Baum, for example, certain parameters introduced in the analysis need not be given specific values for numerical calculations. It is shown in Appendix B that the results obtained here reduce exactly to those of Denison and Baum, as a special case, and that their numerical calculations are restricted to $P = 1$.

Finally, the admittance function is defined as

$$A_b = \left(\frac{u'/u}{p'/\bar{p}} \right)_{x \rightarrow \infty},$$

the right-hand side to be evaluated at the downstream (chamber) side of the burning region. Because of the identity

$$\frac{m'}{\bar{m}} = \frac{u'}{\bar{u}} + \frac{\rho'}{\bar{\rho}},$$

and since $\rho'/\bar{\rho} \rightarrow p'/\gamma\bar{p}$ when the waves are assumed to be isentropic, the admittance function is

$$A_b = \left(\frac{m'/\bar{m}}{p'/\bar{p}} \right)_{x \rightarrow \infty} - \frac{1}{\gamma}. \quad (42)$$

According to the quasi-static approximation, $(m'/\bar{m})_{x \rightarrow \infty} = m'_s/\bar{m}$. The results will therefore be discussed for the mass flux itself, given by (41). The real part of the ratio $[(m'/\bar{m})/(p'/\bar{p})]_{x \rightarrow \infty}$ is often denoted by the symbol μ/ϵ .

Some Numerical Results

The real part of Eq. (41) is

$$\frac{1}{n\epsilon} = \frac{D[P - (E/n)(X_p + X_{p-r})] - (X_{-i})(X_{p-i})}{D^2 + (X_{-i})^2} + \frac{n_s}{n} \quad (43)$$

$$D = X_{-r} - X_{-o} + (1 - n_s/n)^{-1} \times \left[P - \frac{E}{n}(X_p + X_{p-o}) \right] \quad (44)$$

where $()_r, ()_i$ denote real and imaginary parts, and the explicit formulas for the various quantities involved are given in Appendix D. A similar result is obtained for the imaginary part of (41), but it is not discussed here for reasons given before. However, the imaginary part does affect the frequency of oscillations driven by burning in a chamber [7], a fact which should perhaps be considered, for example, in the reduction of data obtained from T-burners.

Since there are a large number of parameters, the numerical results are potentially very extensive. Only a sufficient amount will be presented here to gain an idea of the importance of some of the variables. The primary independent variable is the dimensionless frequency, ω_p , based on the characteristic time for heat conduction in the solid phase. For typical propellants, $\omega_p = 5$ corresponds to frequencies in the range from a few hundred to several thousand cycles per second; the range of frequency is most strongly affected by the mean burning rate. More significantly, the separate regions treated here are each characterized by one or more dimensionless parameters, as listed in Table 1. Note that the gas phase introduces

Table 1. A list of the important parameters

| Region | Parameter | Interpretation |
|---------------|-----------------------------|---------------------------|
| Decomposition | l | thickness |
| | Q | mean heat release |
| | δ_s | temperature sensitivity |
| | α | pressure sensitivity |
| Surface | H | heat of vaporization |
| | \bar{T}_s | surface temperature |
| | E | activation energy |
| | n_s | (temperature sensitivity) |
| | $[A = E(1 - \bar{\tau}_i)]$ | pressure sensitivity |
| Gas phase | P | pressure sensitivity |

only one parameter, P ; others have been eliminated by imposing the limiting behavior, for $\omega \rightarrow 0$ (see Eq. (40)). In particular, also, the flame temperature does not appear, although for a given propellant, its value is probably implied by the values of other quantities which must be specified. It appears explicitly if the assumption of isentropic behavior (7) is not made. There are two other temperatures, the mean surface temperature \bar{T}_s , and the 'conditioning' temperature of the solid, T_i . These arise together only in the ratio $\bar{\tau}_i = T_i/\bar{T}_s$, but \bar{T}_s also occurs in the dimensionless groups of Table 1. The representative values $\bar{T}_s = 900^\circ\text{K}$, $T_i = 300^\circ\text{K}$ are used when necessary. Finally, the pressure index, n , of the mean burning rate law appears alone in several places when the surface and decomposition reactions are taken to be sensitive to pressure changes; it is then given the value $n = \frac{1}{3}$.

It is useful to have a quantitative interpretation of the dimensionless groups listed in Table 1. From their definitions and with the values shown in Table 2, one finds:

$$H = \frac{H_p}{c\bar{T}_s}: H_p = c\bar{T}_s H = 100 H \text{ cal/g}$$

$$A = E(1 - \bar{\tau}_i): E_s = \frac{RT_s}{1 - \bar{\tau}_i} A = 2700 A \text{ cal/mole}$$

$$lQ = \frac{\bar{m}cx}{\lambda_p} \frac{\dot{Q}_d \lambda_p}{\bar{T}_s(\bar{m}c)^2}: x\dot{Q}_d = \bar{m}c\bar{T}_s(lQ) = 450(lQ) \text{ cal/cm}^2\text{-sec}$$

$$\frac{\dot{Q}_d'}{\dot{Q}_d} = \frac{1}{4Q} \left[\delta_s \frac{T_s'}{\bar{T}_s} + \kappa \frac{p'}{\bar{p}} \right]$$

$$\frac{\int_0^\infty \dot{Q}_g' dx}{\int_0^\infty \dot{Q}_g dx} = \frac{1}{Q_g} \left[q_1 \frac{T_s'}{\bar{T}} + \left\{ \frac{n}{E} \frac{c}{c_p} P + \frac{\gamma - 1}{\gamma} \bar{\tau}_c' \right\} \frac{p'}{\bar{p}} \right]$$

Table 2. Numerical values

| |
|--|
| $\lambda_p = \lambda_g = 5 \times 10^{-4} \text{ cal/g-cm-}^\circ\text{K}$ |
| $\rho_p = 1.5 \text{ g/cm}^3$ |
| $\bar{\rho}_c = 10^{-4} \bar{p}$ (\bar{p} in atmospheres) g/cm^3 |
| $\frac{c_p}{T_s} = c = 0.33 \text{ cal/g-}^\circ\text{K}$ |
| $\bar{T}_s = 900^\circ\text{K}$ |
| $T_i = 300^\circ\text{K}$ |

where Q_g now stands for dimensionless total heat release in the gas phase. Thus, $H = 1$ implies a heat of vaporization of 100 cal/g; $A = 3, 10$ give surface activation energies of 8100, 27,000 cal/mole; $l = 1$, $Q = 0.01$ means a mean energy release in the decomposition region of 4.5 cal/sec per cm^2 of propellant surface; $l = 1$ implies a thickness of the decomposition region of something less than 10μ or so; $Q = 0.01$, $\delta_s = \kappa = 0.05$ and 1 per cent fluctuations in pressure and surface temperature give a 1 per cent change in energy release in the decomposition region; and $P = 1, E = 4.5$ or $P = 6, E = 15$ provide approximately a 1 per cent change in the total heat release in the gas phase for $Q_g = 0.01$. The last value implies a total heat release of approximately 500–1000 cal/g-sec in the gas phase.

Some computed results are shown in Figs. 3–9. So far as comparison with experimental results and the general stability problem are concerned, the position and magnitude of the peak are the primary concern. It happens, as discussed also in the next section, that the peaks occur for increasing values of frequency as the activation energy (or A) is increased. Simultaneously, the value of P must be increased. That is, in order for a propellant having a relatively higher value of surface activation energy to exhibit a peak in its response function, the gas phase reactions must be relatively more sensitive to pressure changes. This sensible result may be seen by comparing Figs. 3 ($A = 3, P = 1$) and 7 ($A = 10, P = 6$). The curve

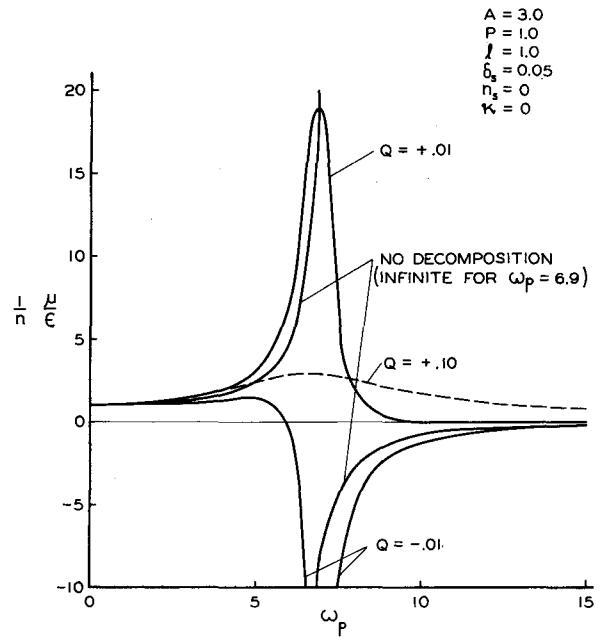
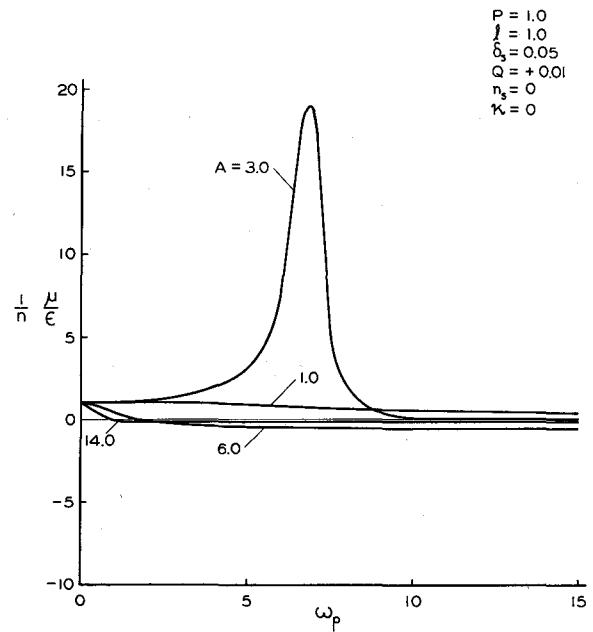


FIG. 3. Effect of decomposition.

FIG. 4. Influence of surface activation energy for $P = 1$.

shown for no decomposition in Fig. 3 corresponds to a curve given by Denison and Baum in their Fig. 2, except that they show the magnitude of $(m'_s/\bar{m})/n(p'/\bar{p})$, not the real part.

For $A = 3, P = 1$, and $A = 10, P = 6$, μ/ϵ becomes infinitely large at a frequency given by Eq. (47) in the following section, if there is no decomposition and $n_s = 0$. Indefinitely large values are of course not observed experimentally, nor is the general shape (large positive followed by large negative values)

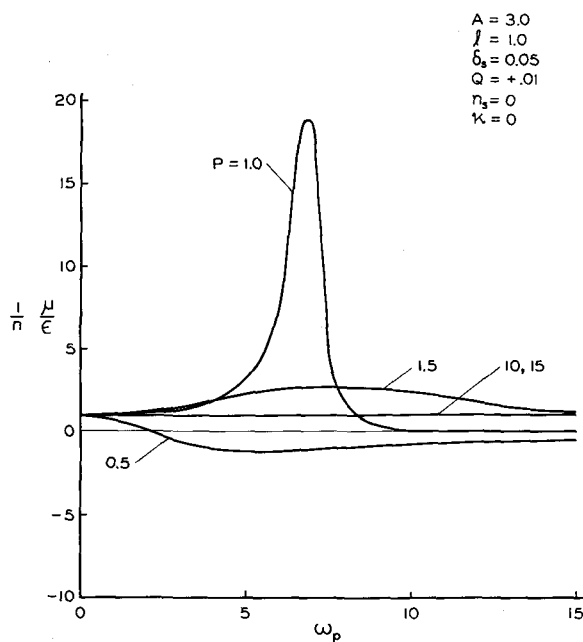


FIG. 5. Influence of gas phase sensitivity for $A = 3$ (surface activation energy 8100 cal/mole).

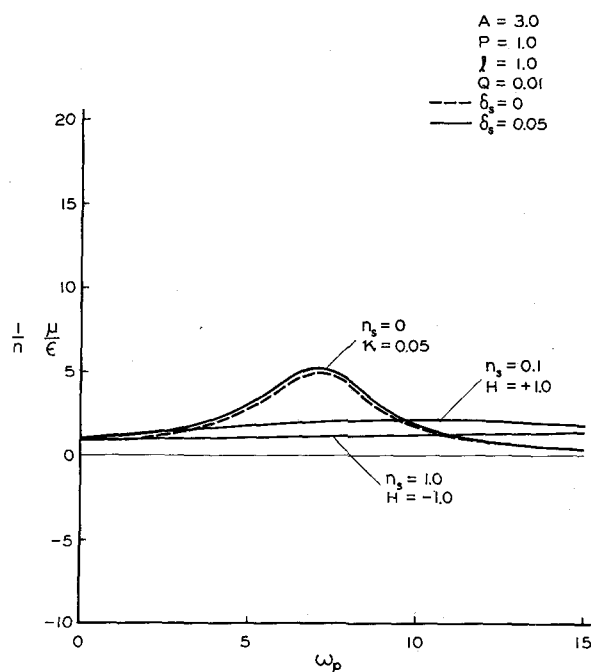


FIG. 6. Effect of pressure sensitivity of decomposition and surface reaction

found in the measurements reported. This behavior is not found in the analysis when decomposition is included, as Figs. 3 and 7 show.

On the other hand, for the higher values of A , which correspond to more reasonable values of surface activation energy, there are values of P for which

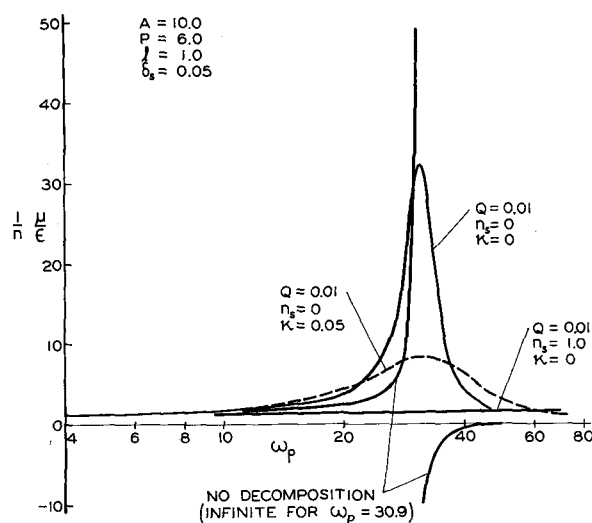


FIG. 7. Effect of decomposition and surface reactions sensitive to pressure (high A and P).

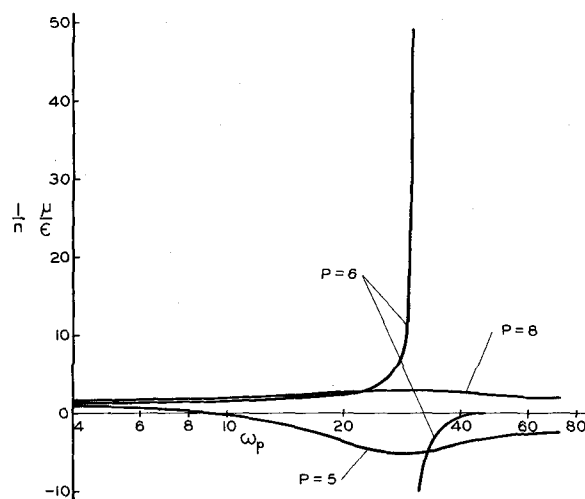


FIG. 8. Influence of gas phase sensitivity for $A = 10$ (no decomposition).

there is only a smooth positive peak not followed by negative values, even if decomposition is ignored. However, as in Figs. 7 and 8, these occur at frequencies for which the quasi-static assumption for the behavior of the gas phase may be suspect. The condition is that $\omega_g \approx (\bar{p}_c / \rho_p) \omega_p$ be much less than unity. For $\rho_p = 1.5 \text{ g/cm}^3$, molecular weight of gases 25, and a chamber temperature of 2100°K , $\bar{p}_c / \rho_p \approx 10^{-4} \bar{p} \text{ g/cm}^3$ with \bar{p} in atmospheres. Hence when $\omega_p = 40$, the quasi-static analysis should work well only for a mean chamber pressure less than, say, 50 atm.

Although peaks can be found for 'reasonable' values of the surface activation energy—namely, those which seem to be associated with the steady burning process—too much emphasis should not be placed on this result. The quantity E (or E_s) is a

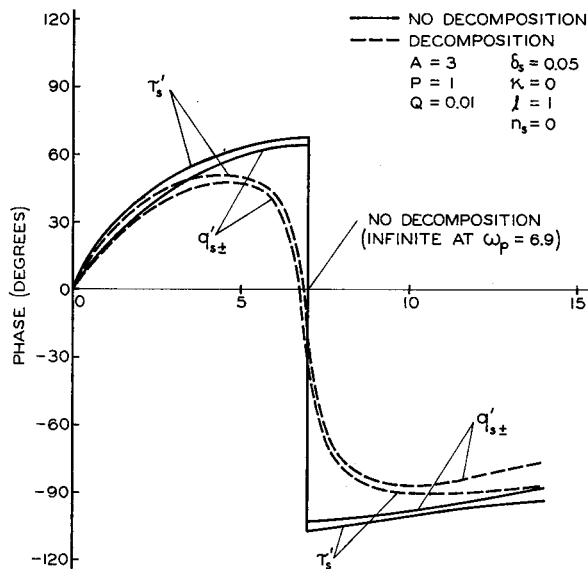


FIG. 9. Phases of surface temperature and heat transfer with respect to pressure oscillations.

measure of the sensitivity of the surface reaction to temperature changes and happens to be the 'activation energy' if an Arrhenius law is used. But, as already remarked in connection with Eq. (10), this may be only part of the story. In addition to possible phase lags, under dynamical conditions, the character of the surface—roughness, inhomogeneity, or even the chemistry itself—may be substantially different from that existing in the steady state. Thus, one should perhaps not be too concerned if it should happen that the values of E required to match data for the response function do not agree particularly well with those inferred from steady burning.

It is an interesting result that a positive peak is obtained, when decomposition is included, only if the decomposition reaction is exothermic. This seems to be generally the case, irrespective of the values assigned to other parameters in the problem. As Eq. (41) shows, all results for μ/ϵ are independent of the latent heat H_p for the surface reaction, if the sensitivity of the surface reaction to pressure changes is ignored (see a comment following Eq. (41)). Note that the sensitivity of both the surface and the decomposition reactions has been ignored in Figs. 3–5.

Moreover, there is only a weak dependence on the value of δ_s , the sensitivity of decomposition to temperature. The curves for $\delta_s = 0$ differ only slightly from those for $\delta_s = 0.05$, as shown later in Fig. 6. Results for $\delta_s = 0$ have not been included in order to keep the drawings simple. Evidently the importance of the decomposition lies mainly in its effect on the mean temperature profile, which in turn affects the heat transfer away from the solid–gas interface both

in the steady state and when the surface position oscillates (through the second term in Eq. (13)). From (16), (17), and (18), it is easy to show that although the mean temperature at $\xi_p = -l$ is not greatly different in the two cases (decomposition versus no decomposition), the mean heat transfer is roughly e^l times as large when there is decomposition. The fluctuations in heat transfer (q'_{s+} , q'_{s-}) are even more strikingly affected. For example, the magnitude of q'_{s-} (the loss to the solid phase) is approximately $\frac{1}{6}$ as large, at $\omega_p = 7$, for the case $Q = +0.01$ in Fig. 3, as it is for no decomposition. The phase between q'_{s+} and p'/\bar{p} is also strongly affected.

It is probably significant that for most of the parameters there seems to be a range in which the response is most enhanced. Thus, if Q or l is too large (say, $Q = 1$ or $l = 10$), μ/ϵ becomes unreasonably small. As Figs. 5 and 8 show, if all other parameters are fixed, the response is sharply peaked only for a restricted range of P .¹ A similar statement applies to A , illustrated in Fig. 4. Incidentally, for the values of P and A involved, the fluctuation of energy release in the gas phase is of the order of 10–20 cal/cm²-sec, roughly the same as that in the decomposition region.

Another important question concerns the sensitivity of the decomposition and surface reactions to pressure. It appears, as the example of Fig. 6 shows, that in either case, the peaked portion of the response is reduced, although it may still have values comparable to those observed in experiments. This is rather a surprising result. Although, as Eq. (39) shows, the response is increased if the mass release is proportional to the pressure fluctuation, this direct effect is more than compensated by a decrease of the surface temperature, given by Eq. (38). The reason for this seems to be that the mass released carries energy with it, thereby cooling the surface. On the other hand, if the decomposition region responds directly to pressure changes, this leads to increased heat loss from the surface to the solid; the loss (i.e. q'_{s-}) then depresses the response.

'Intrinsic Instability' and Peaks of the Response Function

Several previous investigators [1, 2] have dwelt upon the existence of strictly unstable motions ('self-excited' or 'intrinsic' modes), which can be found in the analysis if the frequency is permitted to be complex, with a negative real part. The boundary between stable (or steady harmonic) and unstable

¹ Within this range, μ/ϵ has a single positive peak for some values of P , and a positive peak followed by a negative peak for others.

motions is determined by the vanishing of the denominator of (38) or (39). This condition, which, obviously, is also found if the problem is solved by use of the Laplace transform [1], has a rather simple interpretation which seems not to have been previously noted. Both the real and imaginary parts must vanish simultaneously,

$$X_{-i} = 0 \quad (43)$$

$$X_{-r} - X_{+} + X_s = 0. \quad (44)$$

The first condition means that the heat transfer to the solid phase from the burning interface must be in phase with the temperature. After substitution of the formulas (30) and (35) into the energy balance (37), one has

$$[X_{-} - X_{+} + X_s]\tau'_s - \left[\frac{n}{E}P - (X_p + X_{p-}) \right] \frac{p'}{\bar{p}} = 0.$$

If (44) as well as (43) is satisfied, then for $p'/\bar{p} = 0$, conservation of energy at the burning surface is assured by that part of the total net energy flux which depends on temperature fluctuations only. Hence, if there is a small pressure fluctuation (and the coefficient of p'/\bar{p} is non-zero as it is in general), the associated contribution to the surface energy flux can be compensated only by an infinitely large fluctuation of surface temperature. This is then manifested in an infinitely large value of the response function μ/ϵ .

Another way of looking at the peaks is based on the following interpretation of the response function. Suppose one starts with the premise that the surface mass flux, $M = m_s/\bar{m}$ is a function of the surface temperature and the pressure. Then a small change $dM = \mu^1$ is given formally by

$$dM = \mu = \left(\frac{\partial M}{\partial \tau_s} \right)_\epsilon \tau'_s + \left(\frac{\partial M}{\partial p/\bar{p}} \right)_{\tau_s} \epsilon \quad (45)$$

where $\epsilon = p'/\bar{p}$ and $\tau'_s = T'_s/\bar{T}_s$ as before. Now a small change of surface temperature can also, ultimately, be related to ϵ , but subject always to the conservation of energy at the surface (namely Eq. (37)). Define

$$Q_s = \frac{c_p}{c} q'_{s+} - q'_{s-} = (X_{+} - X_{-}) \tau'_s + \left(\frac{c_p}{c} q_2 - X_{p-} \right) \bar{u}$$

as the fluctuation of net heat transfer to the surface and

$$E_s = -(X_s \tau'_s + X_p \epsilon)$$

as the net energy transported to the surface (hence, the negative sign) associated with a fluctuation of mass transfer. Thus, τ'_s can be considered a function of ϵ only, but subject to the constraint of Eq. (39), namely, $\mathcal{E} = Q_s + E_s = 0$. Formally, then,

$$\tau'_s = \left(\frac{\partial \tau_s}{\partial \epsilon} \right)_\epsilon \epsilon$$

and (45) becomes

$$\mu = \left[\left(\frac{\partial M}{\partial \tau_s} \right)_\epsilon \left(\frac{\partial \tau_s}{\partial \epsilon} \right)_\epsilon + \left(\frac{\partial M}{\partial \epsilon} \right)_{\tau_s} \right] \epsilon. \quad (46)$$

But from Eq. (10), $(\partial M/\partial \tau_s)_\epsilon = E$ and $(\partial M/\partial \epsilon)_{\tau_s} = n_s$. Moreover, use of a formula for partial derivatives gives

$$\begin{aligned} \left(\frac{\partial \tau_s}{\partial \epsilon} \right)_\epsilon &= - \frac{(\partial \mathcal{E}/\partial \epsilon)_{\tau_s}}{(\partial \mathcal{E}/\partial \tau_s)_\epsilon} \\ &= - \frac{(\partial Q_s/\partial \epsilon)_{\tau_s} + (\partial E_s/\partial \epsilon)_{\tau_s}}{(\partial Q_s/\partial \tau_s)_\epsilon + (\partial E_s/\partial \tau_s)_\epsilon} \end{aligned}$$

which, in view of the above definitions of Q_s and E_s , becomes

$$\left(\frac{\partial \tau_s}{\partial \epsilon} \right)_\epsilon = - \frac{[(c_p/c) q_2 - X_{p-}] - X_p}{(X_{+} - X_{-}) - X_s}.$$

Substitution for the partial derivatives in (46) leads to

$$\frac{\mu}{\epsilon} = E \frac{(c_p/c) q_2 - (X_p + X_{p-})}{X_{-} - X_{+} + X_s} + n_s$$

which, as it must, agrees with Eq. (39).

Now referring to (46), one sees that μ/ϵ becomes indefinitely large when $(\partial \tau_s/\partial \epsilon)_\epsilon$ does so. That is, if, when the net surface energy transfer \mathcal{E} is constant (in fact, $\mathcal{E} = 0$ is required), a small change of pressure results in an infinitely large change of surface temperature, μ also becomes infinitely large unless the surface activation energy vanishes. This is, of course, merely a restatement of the argument based on Eqs. (43) and (44), but it may be of interest to put the formula for the response function in the form (46).

Some authors have discussed these unstable motions without reference to the frequency response. In fact, the greatest peak in the response occurs when the conditions (43) and (44) are as closely met as possible for the chosen values of the parameters. One way of determining this fact is to look at the phases, with respect to the pressure oscillation, as shown in Fig. 9, for example. Very close to the frequency at which the peak occurs, the oscillations of surface temperature, and the heat transfer on both sides of the surface, become real quantities (i.e. the phase is zero), although not at the same values of the

¹ In this section, μ will be used for $(m'_s/\bar{m})/(p'/\bar{p})$, not simply the real part.

frequency. If there is no peak, the imaginary parts of these functions are always of the same sign.

For the general case, with decomposition and pressure sensitivity included, there is no simple analytical formula for the position of the peak. However, it happens that the frequency at which the highest peak occurs (as A and P are varied), no matter what complications are included, is not very different from the frequency at which μ/ϵ becomes infinite for the simplest case of no decomposition. The situation seems to be roughly similar to a resonance condition in a mechanical system. An infinitely large response is avoided by the presence of damping, which, however, does not much alter the frequency associated with the maximum response. Here, for example, decomposition acts as a kind of damping mechanism and depresses the response, but as Figs. 3 and 7 show, the frequency of peak is not significantly changed. Now for no decomposition and $n_s = 0$, Eq. (41) becomes

$$\frac{1}{n} \frac{m'_s/\bar{m}}{p'/\bar{p}} = \frac{P}{[\lambda + (A/\lambda)] - (1 + A) + P}$$

and for the denominator to be zero,

$$\lambda(\lambda - 1) + \lambda(P - A) + A = 0. \quad (47)$$

The equation for λ is $\lambda(\lambda - 1) = i\omega_p/4$, and after substitution into (47), the real and imaginary parts are

$$\lambda_r = \frac{A}{A - P}, \quad \lambda_i = \frac{\omega_p/4}{A - P}. \quad (48)$$

Also, the equation for λ itself gives

$$\lambda_r^2 - \lambda_i^2 = \lambda_r, \quad \lambda_i(2\lambda_r - 1) = \omega_p/4. \quad (49)$$

Substitution of (48) into the first of (49) gives

$$\omega_p = 4(AP)^{\frac{1}{2}} \quad (50)$$

for the frequency at which μ/ϵ becomes infinite. However, A and P are not independent for this condition, since substitution of (48) into the second of (49) gives

$$(A - P)^2 = A + P. \quad (51)$$

Thus, if, for example, one chooses A , then P is found from (51), and (50) gives the frequency. In this way, one can locate very simply where the frequency response is indefinitely large. Of course, if A and P are not chosen so as to satisfy (51), then the response (for real ω_p) nowhere becomes infinite. But there may

be maximum values, located in frequency by the condition that $d(\mu/\epsilon)/d\omega_p = 0$; their positions depend on both A and P .¹

The point here is that for a given value of A , the largest peak in the response can be found by using (50) and (51). If decomposition is included, the peak is not infinite, but it does occur very nearly at the same frequency. The approximation is, however, less good when the pressure sensitivity of the reactions is included.

It must be emphasized that the existence of a zero in the denominator of μ/ϵ is not a necessary condition for the existence of standing waves in a chamber (contrary to a view offered in some earlier work, [2], for example). The question of whether or not such modes can be sustained requires study of the complete problem, including mean motions within the chamber; and a positive answer is possible even if the unstable roots are not found [7].

Concluding Remarks

The results summarized here are of course far from complete, although most of the dominant trends are illustrated. It seems better to perform extensive numerical work only when experimental results are to be interpreted. The limited calculations carried out indicate that there should be no difficulty obtaining agreement with measurements, simply by proper choice of the various parameters. But that is by no means a satisfactory conclusion.

The real aim is to be able to classify propellants according to the behavior characterized by the various dimensionless parameters found here. It may then be possible to ascribe certain aspects of the behavior to the separate regions of the burning process. Ultimately one would then like to trace the features found experimentally, and (optimistically) described at least qualitatively by a theoretical model, to the composition of the propellant. A difficulty with the analysis presented here may be that there are too many parameters. Thus, if one begins with the simplest limiting case (case I), originally treated by Denison and Baum, there are, beside ω_p , only two parameters: A , characterizing the surface, and P , characterizing the gas phase. Two more parameters arise if the surface reaction is permitted to be sensitive to pressure changes (case II): n_s , the pressure index for the reaction, and H , the latent heat. With n_s non-zero, the response is reduced compared to case I and, depending

¹ These peaks in $|m'_s/\bar{m}|$ have been called 'resonances' by Denison and Baum, as opposed to the infinitely large values associated with the 'self-excited' or 'intrinsic' instability.

on the values and sign of H (i.e. exothermic or endothermic surface reaction), μ/ϵ may decrease rather than increase with frequency, near $\omega = 0$. Finally (case III), there are at least four more parameters associated with the decomposition region: the thickness l , the mean heat release Q , the sensitivity to temperature δ_s , and the sensitivity to pressure κ . For the conditions examined, the presence of decomposition always results in reduced values of the response peaks. But, unless Q is quite large, the response seems not to be broadened quite so much as in case II. It has already been noted that δ_s is relatively unimportant and can probably be ignored.

For all cases, the primary independent variable used here is ω_p , which is inversely proportional to the square of the burning rate. It therefore contains probably the strongest, and certainly the most explicit dependence on mean pressure. Thus, for example, with all other parameters fixed, the peak of the response will be shifted to higher real frequencies when the mean pressure is increased (since the peak will occur at a fixed value of $\omega_p \sim \omega/r^2$). If such a shift is not observed, then one might conclude that other parameters depend on the pressure. In particular, the position and size of the peak can be altered by changing A and P (compare Figs. 3 and 7), broadened by taking Q , l , κ , $n_s \neq 0$ and so forth. Naturally one should not expect, or even attempt, to obtain extensive quantitative agreement—the model certainly cannot accommodate all details of the problem.

Indeed, many important characteristics have been greatly simplified. Heterogeneous properties of the solid have, essentially, been ignored; temperature dependence of properties is not accounted for; diffusion in the gas phase is not included (explicitly), etc. Even so, there is a great deal of freedom afforded in applying the results to experiment. It seems best not to complicate the picture further, at least so far as the solid phase is concerned. In respect to the gas phase, one may wish to consider a more involved analysis, which would fit into the scheme developed here, but with different functions X_+ , X_p . Perhaps the most important correction would be to extend the calculation to higher frequencies; at present, only the very complicated treatment of [3] is valid outside the 'quasi-static' region.

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Appendix A

With $\delta\xi_l = \xi_{pd} + l$, and the appropriate derivatives of the mean temperature profile computed from Eqs. (16) and (17), eq. (14) gives

$$\tau'_{l+} = -\delta\xi_l A_l = \tau'_{l-}.$$

Thus, one relation between A_1 , A_2 , A_3 is obtained by equating (26) and (27) at the decomposition interface:

$$A_1 e^{-\lambda_1 l} = A_2 e^{-\lambda_1 l} + A_3 e^{-\lambda_2 l} - \frac{i}{\omega_p} \left[\delta_s \tau'_s + \kappa \frac{p'}{p} \right]. \quad (A1)$$

When normalized, Eq. (15) is

$$q'_{l-} - \tau'_{l-} = q'_{l+} - \left(1 + \frac{Q}{A_l}\right) \tau'_{l+}$$

and by differentiating (26) and (27) one has

$$\begin{aligned} q'_{l-} &= \lambda_1 A_1 e^{-\lambda_1 l} \\ q'_{l+} &= \lambda_1 A_2 e^{-\lambda_1 l} + \lambda_2 A_3 e^{-\lambda_2 l} \end{aligned}$$

The last three equations give

$$\begin{aligned} A_1 e^{-\lambda_1 l} (\lambda_1 - 1) &= A_2 e^{-\lambda_1 l} \left(\lambda_1 - 1 - \frac{Q}{A_l} \right) \\ &+ A_3 e^{-\lambda_2 l} \left(\lambda_2 - 1 - \frac{Q}{A_l} \right) \\ &- \frac{i}{\omega_p} \left(1 + \frac{Q}{A_l} \right) \left(\delta_s \tau'_s + \kappa \frac{p'}{p} \right). \quad (A3) \end{aligned}$$

Now eliminate $A_1 e^{-\lambda_1 l}$ from (A1) and (A3) to find

$$A_3 = A_2 \alpha - \frac{i\beta}{\omega_p} \left[\delta_s \tau'_s + \kappa \frac{p'}{p} \right] \quad (A4)$$

where α and β are defined after Eq. (29).

At the solid-gas interface, (27) gives the temperature

fluctuation

$$\tau'_{o-} = A_2 + A_3 - \frac{i}{\omega_p} \left[\delta_s \tau'_s + \kappa \frac{p'}{p} \right]$$

and A_2 can be found by substituting (A4) into this equation:

$$A_2 = \frac{1}{1 + \alpha} \left[\tau'_o + \frac{i}{\omega_p} (1 + \beta) \left(\delta_s \tau'_s + \kappa \frac{p'}{p} \right) \right]. \quad (\text{A5})$$

The fluctuation of heat transfer at the interface is, from (27),

$$q'_{o-} = \lambda_1 A_2 + \lambda_2 A_3.$$

With A_2 and A_3 given by (A4) and (A5), the final result is Eq. (29).

Appendix B

The most important difference between this analysis, in the limiting case of no decomposition, and the work of Denison and Baum (D.B.) is that they integrated the energy equation twice to obtain an explicit expression for the temperature profile. Hence it is interesting to find that their results are identical with those found here, which rest on a single integration augmented by the assumption (34); the temperature is therefore not determined. With x normalized to ξ_g and $\tau' = T'/\bar{T}_s$, the perturbed form of D.B.'s Eq. (21), which is their first integral of the energy equation, is

$$\left(\frac{d\tau'}{d\xi_g} \right)_{s+} = q'_{s+} = -\frac{m'_s}{\bar{m}} \left[\frac{\bar{T}_f}{\bar{T}_s} - 1 - \frac{Q_r \epsilon_r}{C_p \bar{T}_s} \right] - \frac{T'_f}{\bar{T}_s} + \frac{T'_s}{\bar{T}_s} \quad (\text{B1})$$

where T'_f is the fluctuation of the flame temperature. The perturbation of their second integral of the energy equation is their Eq. (29), here normalized with respect to \bar{T}_s :

$$\frac{T'_f}{\bar{T}_s} = \frac{1}{\mathcal{E}_s} \frac{m'_s}{\bar{m}} - \frac{\bar{n}}{2\mathcal{E}_s} \frac{p'}{p} \quad (\text{B2})$$

where

$$\mathcal{E}_s = (\bar{T}_s/\bar{T}_f) \left(\frac{\bar{n} + 2}{2} + E_f/2R\bar{T}_f \right).$$

Since $m'_s/\bar{m} = E\tau'_s$, substitution of (B2) into (B1) gives

$$q'_{s+} = \tau'_s \left[1 - \frac{E}{\mathcal{E}_s} - E \left\{ \frac{\bar{T}_f}{\bar{T}_s} - 1 - \frac{Q_r \epsilon_r}{C_p \bar{T}_s} \right\} \right] + \frac{\bar{n}}{2\mathcal{E}_s} \frac{p'}{p}. \quad (\text{B3})$$

This equation may be compared with Eq. (35) here.

Since for no decomposition and no pressure dependence of the surface reaction $n_s = \kappa = Q = l = \delta_s = 0$, and $X_{-o} = 1$, Eq. (40) here gives $X_+ = P - X_s$ so that Eq. (35) is

$$q'_{s+} = \tau'_s \frac{c}{c_p} \left[\frac{c_p}{c} + A - P + E \left(-H + \frac{c_p}{c} - 1 \right) \right] + q_2 \frac{p'}{p}. \quad (\text{B4})$$

The coefficient of τ'_s in (B3) can be rewritten by use of D.B.'s mean energy balance at the surface and their Eq. (27); this step, as noted here after Eq. (40), corresponds to using the limit $\omega \rightarrow 0$ and gives

$$\frac{\bar{T}_f}{\bar{T}_s} - 1 - \frac{Q_r \epsilon_r}{c_p \bar{T}_s} = -\frac{c}{c_p} (1 - \bar{\tau}_i) - \frac{c}{c_p} \left(-H + \frac{c_p}{c} - 1 \right)$$

(D.B. use $L = -H_p$ for the latent heat of the surface reaction). Thus (B3) becomes

$$q'_{s+} = \tau'_s \frac{c}{c_p} \left[\frac{c_p}{c} + A - \frac{E c_p}{\mathcal{E}_s c} + E \left(-H + \frac{c_p}{c} - 1 \right) \right] + \frac{\bar{n}}{2\mathcal{E}_s} \frac{p'}{p}. \quad (\text{B5})$$

Also, D.B. use the parameters α and B :

$$\alpha = \frac{E c_p}{A \mathcal{E}_s c} \quad B = \frac{\bar{n}}{2} (1 - \bar{\tau}_i) = \frac{\bar{n}}{2E} A \quad (\text{B6})$$

Evidently, Eqs. (B4) and (B5) are identical if

$$q_2 = \frac{\bar{n}}{2\mathcal{E}_s} = \frac{c}{c_p} B \alpha \quad (\text{B7})$$

$$P = \frac{E c_p}{\mathcal{E}_s c} = A \alpha \quad (\text{B8})$$

But $P = (E c_p / n c) q_2$ so that (B7) implies

$$P = \frac{E}{n} B \alpha = \frac{E}{n} \cdot \frac{\bar{n}}{2E} A \alpha = \frac{\bar{n}}{2n} A \alpha,$$

which means (B8) is satisfied as well, providing $\bar{n}/2 = n$; this is in fact the case since the linear burning rate, according to D.B. is $r = ap^{n/2}$ (their Eq. (26)). In short, the parameter P in this work is $A\alpha$ in D.B.'s work; they chose $A\alpha = 1$ for the numerical results shown in their Fig. 3.

Since the solution for the solid phase (i.e. q'_{s-}) and the energy matching condition are the same for D.B. and the present work, when there is no decomposition, the identity of q'_{s+} in the two calculations means that the admittance functions are also the same for $P = A\alpha$.

Appendix C

For $\omega_p \rightarrow 0$, the limiting values are:

$$\alpha \rightarrow \alpha_o + i\omega_p \alpha_1 \begin{cases} \alpha_o = -\frac{Q}{Q + \Delta_l} e^{-l} \\ \alpha_1 = \frac{Q}{2(Q + \Delta_l)} \left(l + \frac{\Delta_l}{Q + \Delta_l} \right) \end{cases}$$

$$\beta \rightarrow -1 + \omega_p^2 \beta_2 + i\omega_p \beta_1 \begin{cases} \beta_1 = \frac{1}{4} \left(l + \frac{\Delta_l}{Q + \Delta_l} \right) \\ \beta_2 = \frac{1}{16} \left[l \left(1 + \frac{l}{2} \right) + \frac{\Delta_l(l+1)}{Q + \Delta_l} + \frac{2\Delta_l^2}{(Q + \Delta_l)^2} \right] \end{cases}$$

$$L_1 \rightarrow L_{10} + i\omega_p L_{11} \begin{cases} L_{10} = \frac{1}{1 + \alpha_o} \\ L_{11} = \frac{1}{1 + \alpha_o} \left[\frac{1}{4} (1 - \alpha_o) - \frac{\alpha_1}{1 + \alpha_o} \right] \end{cases}$$

$$L_2 \rightarrow L_{20} + i\omega_p L_{20} \begin{cases} L_{20} = \delta_s \left(\frac{1}{4} - L_{10} \beta_1 \right) \\ L_{21} = \delta_s \left[\beta_2 L_{10} - \beta_1 \left(\frac{1}{4} + L_{11} \right) - \frac{1}{16} \right] \end{cases}$$

$$A_1 \rightarrow A_{10} + i\omega_p A_{11} = (L_{10} + L_{20}) + i\omega_p (L_{11} + L_{22})$$

With these results, it is easy to find the limiting values of X_- and X_{p-} :

$$X_{-o} = L_{10} + L_{20} + 4EA_{11}[(Q + \Delta_l)e^l - Q],$$

$$X_{p-o} = \frac{\kappa}{\delta_s} L_{20} + 4n_s L_{11}[(Q + \Delta_l)e^l - Q].$$

Appendix D

$$X_{-r} = A_{1r} + 4E(s_1 - Q) \frac{L_{1i}}{\omega_p}$$

$$X_{-i} = A_{1i} - \frac{4E}{\omega_p} [(L_{1r} - 1)s_1 - L_{1r}Q]$$

$$X_{p-r} = \frac{\kappa}{\delta_s} L_{2r} + \frac{4n_s}{\omega_p} L_{1i}(s_1 - Q)$$

$$X_{p-i} = \frac{\kappa}{\delta_s} L_{2i} - \frac{4n_s}{\omega_p} [(L_{1r} - 1)s_1 - L_{1r}Q]$$

$$L_{1r} = \frac{B_1(1 + \alpha_r) + B_2\alpha_i}{(1 + \alpha_r)^2 + \alpha_i^2}$$

$$L_{1i} = \frac{B_2(1 + \alpha_r) - B_1\alpha_i}{(1 + \alpha_r)^2 + \alpha_i^2}$$

$$L_{2r} = \frac{\delta_s}{\omega_p} [\beta_i(1 - \lambda_{1r}) - \beta_r\lambda_{1i}(1 + \beta_r) - \beta_i L_{1r}]$$

$$L_{2i} = \frac{\delta_s}{\omega_p} [L_{1r}(1 + \beta_r) - L_{1i}\beta_i - \beta_r(1 - \lambda_{1r}) - \beta_i\lambda_{1i}]$$

$$\alpha_r = Z \frac{A_1 A_3 + A_2 A_4}{A_3^2 + A_4^2}$$

$$\alpha_i = Z \frac{A_2 A_3 - A_1 A_4}{A_3^2 + A_4^2}$$

$$\beta_r = \frac{Y}{A_3^2 + A_4^2} [A_3(A_5 A_6 - \lambda_{1i} A_7) + A_4(A_5 A_7 + \lambda_{1i} A_6)]$$

$$\beta_i = \frac{Y}{A_3^2 + A_4^2} [A_3(A_5 A_7 + \lambda_{1i} A_6) - A_4(A_5 A_6 - \lambda_{1i} A_7)]$$

$$s_1 = (Q + \Delta_l) e^l$$

$$A_1 = \cos 2\lambda_{1i} l$$

$$A_2 = -\sin 2\lambda_{1i} l$$

$$A_3 = 1 - 2\lambda_{1r} - Q/\Delta_l$$

$$A_4 = -2\lambda_{1i}$$

$$A_5 = \lambda_{1r} + Q/\Delta_l$$

$$A_6 = \cos \lambda_{1i} l$$

$$A_7 = -\sin \lambda_{1i} l$$

$$B_1 = \lambda_{1r} + \alpha_r(1 - \lambda_{1r}) + \alpha_i \lambda_{1i}$$

$$B_2 = \lambda_{1i} + \alpha_i(1 - \lambda_{1r}) - \alpha_r \lambda_{1i}$$

$$Y = \exp[(1 - \lambda_{1r})l]$$

$$Z = \frac{Q}{\Delta_l} \exp[(1 - 2\lambda_{1r})l]$$

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